

## REMOVING THE CADMIUM, ARSENIC AND SULFATE IONS FROM WET PROCESS PHOSPHORIC ACID

M. ABDALBAKE and O. SHINO

Atomic Energy Commission  
Hydrometallurgy office  
P.O.Box 6091, Damascus, Syria

Received: Mai 17, 2004

### Abstract

Commercially, phosphoric acid is manufactured using different processes. The wet-process is the process applied in Syria using phosphate mineral, and phosphoric acid produced by this process contains a variety of impurities.

This paper studies the precipitation of Cd, As and sulfate ions. The results show that the yield of precipitation of sulfate ion increases by increasing the concentration of barium carbonate and temperature. The precipitation of arsenic increases by increasing the concentration of sodium sulfide and temperature. The precipitation of cadmium was better under ambient temperature by sodium sulfide.

*Keywords:* precipitation, phosphoric acid, cadmium, arsenic.

### 1. Introduction

There has been an increased interest in the past few years in purifying commercial wet phosphoric acid to obtain pure phosphoric acid suitable for food or pharmaceutical uses.

Removal of heavy metals was studied by RUBIO [1] in the adsorptive floatation process for metal ions and dissolved air floatation was employed for the solid/liquid separation and the results showed almost complete removal > 98% of heavy metal ions.

Precipitation of cadmium from phosphoric acid was studied by STENSTROM [2] by using long chain amines as extractants.

SKOROVAROV [3] investigated the extraction of cadmium from phosphoric acid with trioctyl amin.

BECKER [4] mentioned that arsenic was precipitated by sodium sulfide at 58°C. SLACK [5] mentioned that the product acid contains arsenic in the form of arsenious acid,  $\text{As}(\text{OH})_3$ . To eliminate this, the acid is treated with  $\text{H}_2\text{S}$  at 60°C to 80°C.

## 2. Experimental

### 2.1. Materials

Standard cadmium from BDH. Sodium sulfide  $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$  from Riedel–Dehaem with 62%  $\text{Na}_2\text{S}$ . Standard arsenic from BDH. Barium carbonate 99% from Merck. Pure phosphoric acid with 85%  $\text{H}_3\text{PO}_4$  from Merck. Another Syrian commercial phosphoric acid was treated from solid phase with 35%  $\text{H}_3\text{PO}_4$ .

### 2.2. Apparatus and Procedures

Precipitation was carried out in a beaker with a magnetic stirrer placed in a thermostat to control the temperature. The aqueous and solid phases were stirred and were allowed to separate for 20 minutes in a funnel after cooling and filtration. The cadmium and arsenic in the filtered acid were determined by atomic absorption and sulfate ion was measured by the precipitation method [6]. The yield of precipitation of sulfate ion was calculated from the equation:

$$\text{Yield Y} = [(\text{SO}_4) \text{ acid, in} - (\text{SO}_4) \text{ acid, out}] / (\text{SO}_4) \text{ acid, in}$$

where:  $(\text{SO}_4) \text{ acid, in}$  = mass of  $\text{SO}_4$  in the inlet acid  
 $(\text{SO}_4) \text{ acid, out}$  = mass of  $\text{SO}_4$  in the outlet acid

The yield of precipitation of arsenic and cadmium were calculated from the equation:

$$\text{Yield Y} = [(\text{Cd,As}) \text{ acid, in} - (\text{Cd,As}) \text{ acid, out}] / (\text{Cd,As}) \text{ acid, in}$$

where:  $(\text{Cd,As}) \text{ acid, in}$  = mass of Cd,As in the inlet acid  
 $(\text{Cd,As}) \text{ acid, out}$  = mass of Cd,As in the outlet acid

## 3. Results and Discussions

### 3.1. Effect of Concentration of Barium Carbonate

The precipitation of sulfate ion from treated wet phosphoric acid ( $\text{SO}_4 = 1.245$  mass %,  $\text{P}_2\text{O}_5 = 27$  mass %,  $t = 50$  °C). The concentration of barium carbonate was varied from 10 kg/1000 kg acid to 30 kg/1000 kg acid. The results are represented in Fig. 1 in the form yield versus concentration. The results show that the precipitation increases by increasing the concentration of barium carbonate. The optimum concentration of barium carbonate in this condition is 25 kg/1000 kg acid.

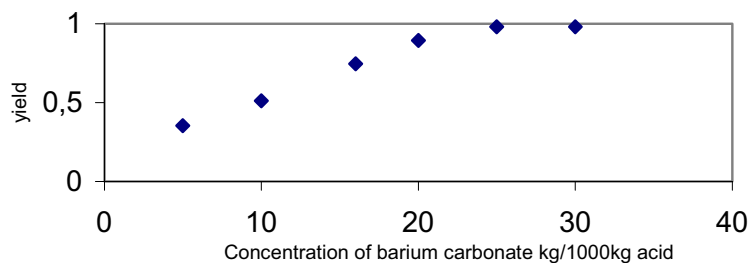


Fig. 1. Effect of concentration of barium carbonate on the precipitation of sulfate ion ( $\text{SO}_4 = 1.235$  mass %,  $t = 50$  °C)

### 3.2. Effect of Temperature on the Precipitation of Sulfate Ion

The effect of temperature was investigated by precipitation of sulfate ion from phosphoric acid using barium carbonate 16 kg/1000 kg acid and the mixing time = 30 minutes but varying the temperature from 25 to 60°C. The results are represented in Fig. 2 in the form of yield versus temperature. The results show that yield increases by an increase in the temperature and the optimum temperature is 55°C.

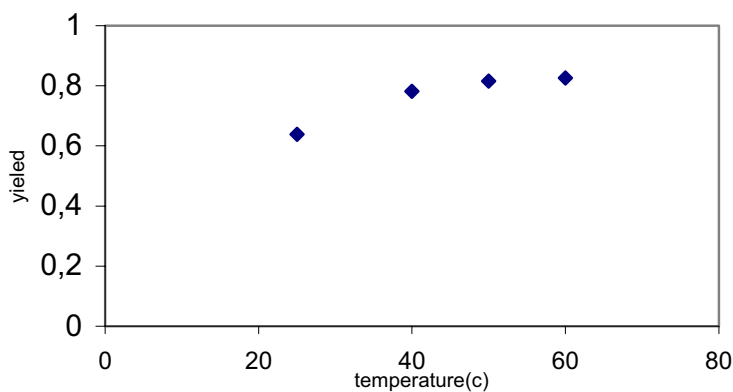


Fig. 2. Effect of temperature on the precipitation of sulphate ion ( $\text{SO}_4 = 1.235$  mass %,  $\text{H}_3\text{PO}_4 = 35$  mass %)

### 3.3. Effect of Mixing Time on the Precipitation of Sulfate Ion

The effect of time of mixing on precipitation was studied. The precipitation was carried out under the conditions ( $t = 55^\circ\text{C}$ , 16 kg  $\text{BaCO}_3$ /1000 kg acid,  $\text{SO}_4 = 1.245$  mass %). The time of mixing was varied from 15 to 60 minutes. The results are represented in Fig. 3 in the form of yield versus time of mixing. The results show that the yield increases from 15 to 50 minutes and remains constant after that.

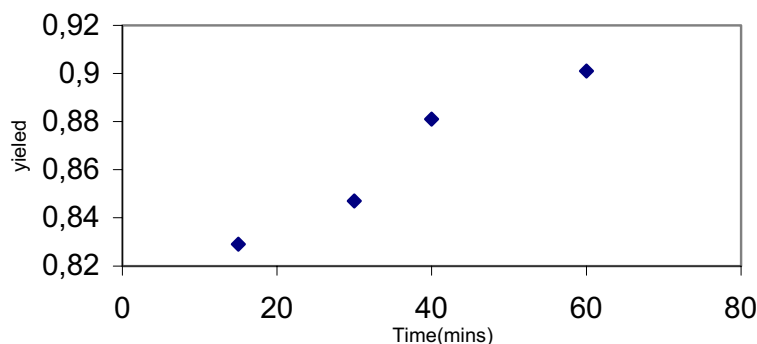


Fig. 3. Effect of mixing time on the precipitation of sulphate ion ( $\text{SO}_4 = 1.235$  mass %,  $\text{H}_3\text{PO}_4 = 35$  mass %)

### 3.4. Effect of Sodium Sulfide on the Precipitation of Arsenic

The precipitation of arsenic was studied using pure phosphoric acid by varying the concentration of sodium sulfide. The phosphoric acid was diluted to 35%  $\text{H}_3\text{PO}_4$ . The arsenic concentration was obtained using a standard solution, prepared by dissolving arsenic in phosphoric acid. The conditions are  $t = 40^\circ\text{C}$ ,  $\text{As} = 40$  mg/l, mixing time is 30 minutes. The concentration of sodium sulfide was varied from 1 kg/1000 kg acid to 6 kg/1000 kg acid. The results are represented in Fig. 4 in the form yield versus concentration. The results show that the precipitation increases by increasing the concentration of sodium sulfide, the optimum concentration of sodium sulfide is 5 kg/1000 kg acid.

### 3.5. Effect of Temperature on the Precipitation of Arsenic

The effect of temperature was investigated by precipitation of arsenic from phosphoric acid using sodium sulfide 5 kg/1000 kg acid and a mixing time of 30 minutes but varying the temperature from 30 to  $60^\circ\text{C}$ . The results are represented in Fig. 5

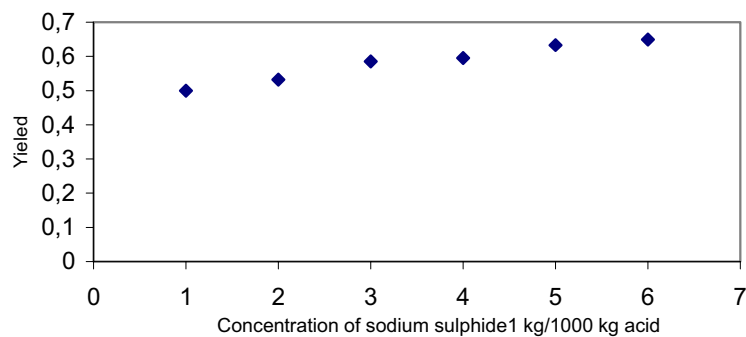


Fig. 4. Effect of concentration of sodium sulfide on the precipitation of arsenic ( $\text{H}_3\text{PO}_4 = 35 \text{ mass } \%$ ,  $\text{As} = 40 \text{ mg/l}$ ,  $t = 40^\circ\text{C}$ )

in the form of yield versus temperature. The results show that yield increases by an increase in the temperature and the optimal temperature is  $55^\circ\text{C}$ .

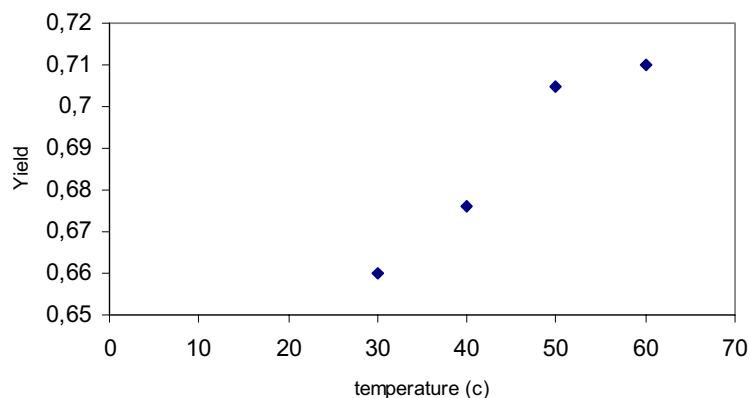


Fig. 5. Effect of temperature on the precipitation of arsenic ( $\text{H}_3\text{PO}_4 = 35 \text{ mass } \%$ ,  $\text{As} = 40 \text{ mg/l}$ ,)

### 3.6. Effect of Mixing Time on the Precipitation of Arsenic

The effect of mixing time was carried out using sodium sulfide 5 kg/1000 kg acid and a temperature of  $55^\circ\text{C}$  but varying the mixing time. The concentration of As was 25 mg/l. The results are represented in Fig. 6 in the form of yield versus mixing

time. The results show that yield increases by an increase in the mixing time and remains constant after 60 °C.

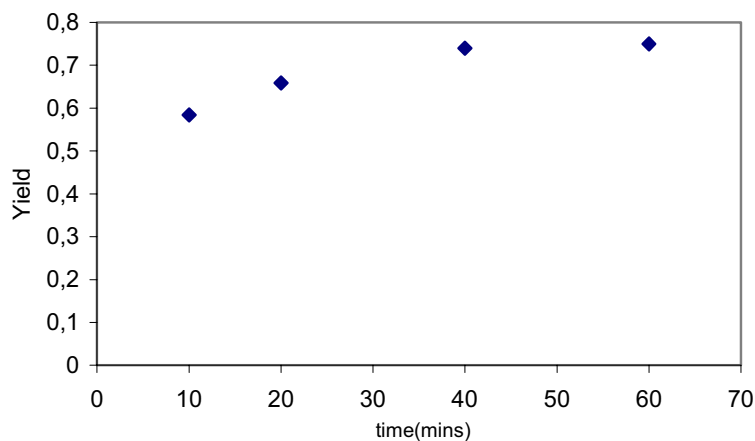


Fig. 6. Effect of mixing time on the precipitation of arsenic ( $\text{H}_3\text{PO}_4 = 35$  mass %,  $\text{As} = 40$  mg/l,  $t = 55$  °C)

### 3.7. Precipitation of Arsenic from Syrian Wet Phosphoric Acid

The precipitation of arsenic from wet phosphoric acid ( $\text{As} = 4$  mg/l) was investigated using sodium sulfide 5 kg/1000 kg acid and a mixing time of 50 minutes and a temperature of 55 °C. The yield of precipitation is 80%.

### 3.8. Effect of Sodium Sulfide on the Precipitation the Cadmium

The precipitation of cadmium was studied using pure phosphoric acid by varying the concentration of sodium sulfide. The phosphoric acid was diluted to 35%  $\text{H}_3\text{PO}_4$ . The cadmium concentration was obtained using a standard solution, prepared by dissolving cadmium in phosphoric acid. The conditions are  $t = 50$  °C,  $\text{Cd} = 110$  mg/l, mixing time is 40 minutes. The results are represented in Fig. 7 in the form yield versus concentration. The results show that the precipitation increases by increasing the concentration of sodium sulfide, the suitable concentration of sodium sulfide is 4 kg/1000 kg.

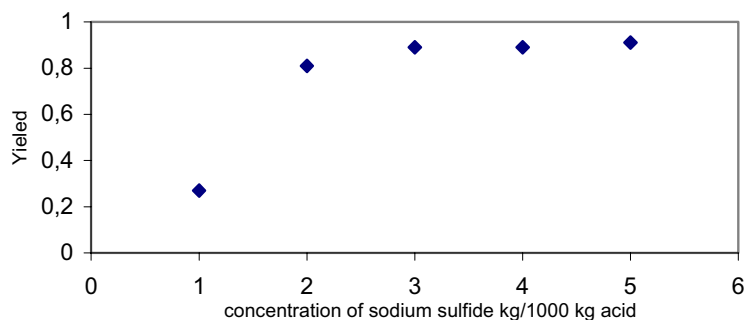


Fig. 7. Effect of concentration of sodium sulfide on the precipitation of cadmium ( $\text{H}_3\text{PO}_4 = 35 \text{ mass } \%$ ,  $\text{Cd} = 110 \text{ mg/l}$ ,  $t = 50^\circ\text{C}$ )

### 3.9. Effect of the Temperature on the Precipitation of Cadmium

The effect of temperature was investigated by precipitation of cadmium from phosphoric acid using sodium sulfide 4 kg/1000 kg acid and a mixing time of 40 minutes but varying the temperature from 25 to 60°C. The results are represented in Fig. 8 in the form of yield versus temperature. The results show that yield decreases by an increase in the temperature and the optimal temperature is 30°C.

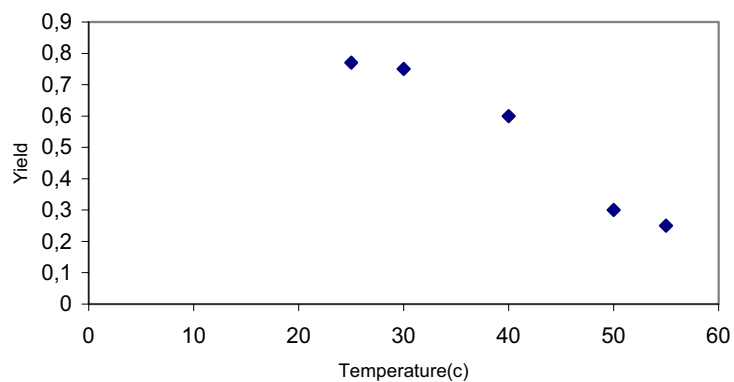
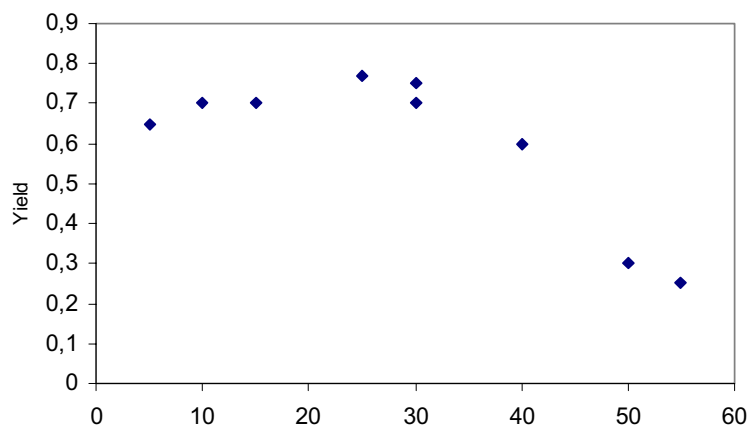


Fig. 8. Effect of temperature on the precipitation of cadmium ( $\text{H}_3\text{PO}_4 = 35 \text{ mass } \%$ ,  $\text{Cd} = 27 \text{ mg/l}$ ,)

### 3.10. Effect of Mixing Time on the Precipitation of Cadmium

The effect of mixing time was carried out by using sodium sulfide 3 kg/1000 kg acid and a temperature of 25 °C but varying the mixing time. The concentration of Cd is 27mg/l. The results are represented in *Fig. 9* in the form of yield versus mixing time. The results show that the precipitation is rapid. The mixing time was fixed at 10 minutes.



*Fig. 9.* Effect of time of mixing on the precipitation of cadmium ( $H_3PO_4 = 35$  mass %,  $Cd = 27$  mg/l,  $t = 25$  °C)

## 4. Precipitation of Cadmium from Syrian Wet Phosphoric Acid

The removal of cadmium from wet phosphoric acid ( $Cd = 4$  mg/l) was investigated using sodium sulfide 5 kg/1000 kg acid and a mixing time of 10 minutes and a temperature of 30 °C. The yield of precipitation is 30%.

## 5. Conclusions

The previous results show that:

1. The precipitation yield for sulphate ion increases rapidly when we use diluted acid and with the increase of the concentration of barium carbonate and that of temperature.
2. The precipitation efficiency for arsenic and cadmium increases by increasing the concentration of sodium sulfide.



3. The arsenic precipitates from diluted acid at 55 °C.
4. The increase of temperature for the precipitation of the cadmium from diluted acid has a negative effect.

### Acknowledgement

The authors would like to express their thanks and appreciation to the General Director of the Syrian Atomic Energy Commission Dr Ibrahim Othman for his help and encouragement to carry out this work.

### References

- [1] RUBIO, J., Removal of Heavy Metal Ions by Absorbative Particulate Flootation, *Minerals Engineering*, **10** No. 7 (1997), pp. 671–679.
- [2] STENSTROM, S., Extraction of Cadmium from Phosphoric Acid Solutions with Amines, *Hydrometallurgy*, **14** (1985), pp. 231–255.
- [3] SKOROVAOV, J. I., Solvent Extraction for Cleaning Phosphoric Acid in Fertilizer Production, *Radioanalytical and Nuclear Chemistry*, **229** Nos. 1–2 (1998), pp. 111–116.
- [4] BECKER, P., *Phosphate and Phosphoric Acid*, Second Edition 1989.
- [5] SLACK, A. V., *Phosphoric Acid*, part 5, 1968.
- [6] Institutul Roman de Standardizare, standard de stas 9267–72.